

and will be used to couple NLO materials to aminated surfaces using techniques we have developed previously.

### 3. Theoretical Investigation of NLO Properties and Characterization

Work here continues, in collaboration with J. K. Baird, in two areas. First we are investigating use of the solvatochromic effect for measuring beta values. This theory is now well in hand, and we are using it to characterize betaines and compounds provided by IBM (our new partner). In the second area we are investigating theoretical calculation of beta values by use of additivity principles and quantum mechanical calculations. This work is just beginning and will be described in more detail in the next report.

Center: Consortium for Materials Development in Space  
The University of Alabama in Huntsville (UAH)

Project Name: "Highly Non-Linear Optical Organic Crystals and Films"

Subproject Name: "Electrooptical Organic Materials"

The University of Alabama in Huntsville

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### Introduction

Nonlinear Optics. Devices employing nonlinear optics (NLO) hold great promise for important applications in integrated optics, optical information processing and telecommunications. Although inorganics are the standard, the exceptional merit of organic materials has now been demonstrated. Properly designed organics possess outstanding optical and electrooptical properties which will substantially advance many technologies including electrooptical switching, optical amplification for communications, and parallel processing for hybrid optical computers.<sup>1</sup> A brief comparison of organic and inorganic materials follows:

Organic (non-resonant)	- - - - -	Inorganic (resonant)
Large reactive nonlinearity	- - - - -	Small reactive part
Fast response (< ps)	- - - - -	Slower response (> 0.5 ns)
Large window (700 - 1600 nm)	- - - - -	Narrower window (a few nm)
Poor processing technologies	- - - - -	Good processing technologies
Amenable to molecular engineering	- - -	Limited prospects for advances

Polydiacetylenes. Special interest has been recently focused on organic small molecules<sup>2</sup> and on organic polymers, such as polydiacetylenes.<sup>3</sup> Ease of design and fabrication is an especially important characteristic with organic polymers. To date several polydiacetylenes with interesting third-order

susceptibilities have been described. Sauteret et. al.<sup>3</sup> found that crystals of the polymeric sulfonate ester called PTS (made from the crystalline diacetylene monomer called TS where R in the structure below is  $\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-p-CH}_3$ ) have third-order susceptibility values comparable to those of inorganic semiconductors or pure germanium.

#### Generalized Diacetylene and Polydiacetylene Structures

Monomer:  $\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$

Polymer:  $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}-\text{C}\equiv\text{C}-\text{C} \\ \diagup \\ \text{R} \end{array}$  etc.

Wegner<sup>4</sup> is credited with pointing out that polydiacetylenes are members of a novel class of polymers; crystals of the monomer polymerize either with uv or x-ray irradiation or thermally to give highly ordered polymer single crystals. Even though the monomer is sensitive to polymerization, the x-ray single crystal structure of the crystalline PTS monomer has been worked out by Enkelmann<sup>5</sup> and the polymer structure has been determined by Kobelt and Paulus.<sup>6</sup> Crystal structures of diacetylene monomers having substituent groups, R, other than the sulfonate ester group have also been studied. Garito et al<sup>7</sup> have prepared a dinitrophenolate derivative, DNP, [ $\text{R} = \text{CH}_2\text{OC}_6\text{H}_3\text{-2,4-(NO}_2\text{)}_2$ ] which thermally polymerizes but does not undergo polymerization under normal x-ray irradiation. Like TS, the crystal structure for the DNP monomer shows that the unsaturated chains of adjacent molecules in the unit cell are positioned so that polymerization requires only slight atomic movement. This is not always the case. It has been demonstrated by several workers that substituent patterns are very important in the molecule's achieving the proper alignment for polymerization.

Knowing that the TS and PTS data require some atomic movement upon polymerization and assuming that the crystal structure probably restricts major atomic reorganization, Baughman<sup>8</sup> suggested that close packing of the monomeric diacetylene residues was essential. A recent report by a group at GTE Laboratories described the properties of thin films prepared by what may be considered a substantially-modified directional solidification device.<sup>9</sup> The description of four-wave mixing experiments, which revealed that indeed these materials have exceptional optical properties<sup>10</sup>, is a significant milestone.

### Technical Discussion

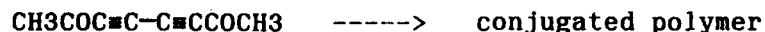
During this period of performance we have focused our attention on the process of growing crystals of polydiacetylenes as thin films. We have discussed in previous reports the problems with this task. For example, the polydiacetylenes with the best nonlinear optical properties, e.g. the toluenesulfonate polymer, typically crystallize as lozenge-shaped crystals rather than as thin films. Crystals have generally been grown from solution of these materials or, in the case of some urethane monomers, from the melt. We decided to devote some attention to defining diacetylene monomers which are less heat sensitive than the toluenesulfonate and which may be processable by a technique other than solution crystallization. This report will dwell only on the crystal growth studies although some chemical structural studies continue to be performed.

Chemical Structural Studies. We undertook studies to see if modification of the diacetylene's chemical structure is a feasible way to make the materials more processable. Tripathy<sup>11</sup> has reported results of a theoretical study which indicated the types of R groups which would best enhance the optical properties

of the diacetylenes. Therefore we sought to take advantage of his studies by targeting molecules which fit his design criteria while having more acceptable vapor pressures for PVT crystal growth. In this connection we have prepared two new diacetylenes which offer some promise. These materials are made from readily available raw materials and readily undergo polymerization when concentrated or crystallized. The first is a diketone, prepared from the corresponding diol by oxidation:

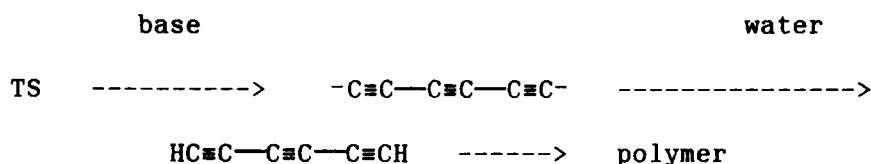


When purified and concentrated, the diacetylenic diketone spontaneously polymerizes to give a dark-colored product.



High pressure liquid chromatography showed the material to be a mixture of monomer, oligomers and polymer. No well defined crystalline phase was present yet the conditions of polymerization were far from ideal. A more controlled polymerization may lead to a better quality material. Laser irradiation of the impure form did not substantially change the amount of polymer but seemed to cause some charring. A second new material was inadvertently prepared in an attempt to replace the tosylate group with other functional groups. Using reaction conditions that we have recently found to be extremely useful for displacement of a sulfonate ester group by good nucleophiles, we attempted to displace a tosylate group with various nucleophiles (e.g. the anions of aromatic amines or alcohols). However, we found that a brownish-black solid was formed which did not incorporate the nucleophile. Thus when we reacted those anionic nucleophiles

or simply the dimethyl sulfide anion ( $\text{CH}_3\text{SOCH}_2^-$ ) in dimethylsulfoxide (DMSO) with the monomeric sulfonate ester TS, we apparently obtained the product of elimination rather than the desired substitution. We can account for the results by assuming that a double elimination and deprotonation has occurred, giving the novel triacetylene dianion, as shown below.<sup>12</sup> When the solution of this material is poured into water, polymerization apparently occurs. Since this new material should have a conjugated structure, it may have useful properties yet unknown. Hence further studies of these new materials, and closely related structures, seems warranted.



We also have attempted to make some other diacetylene monomers that suggest that there is a limit to the extent that we can modify the structure. It appears that certain R groups may be so strongly electron-withdrawing that they will separate from the diacetylene framework and give an ionic residue. This has interesting possibilities, but, at the moment, no commercial interest.

Crystal Growth Studies. Crystal growth studies have been carried out with 3,5-octadiyn-1,8-diol, a low melting diacetylene with better thermal stability than the tosylate. With this monomer crystalline thin films have been deposited on glass, polyethylene film, and on copper. The results so far are doubly impressive. Significantly, we are the first to demonstrate that crystalline monomeric films of diacetylenes can be grown using physical vapor transport techniques. The films are colorless and vary in thickness from about 0.005 mm

to 0.1 mm. Not surprisingly, a great deal of difference is found with the various substrates, with each providing some significant data. To date all experiments have been carried out with continuous pumping and with relatively large differences in temperature between the substrate reservoirs and the growth surface. However, much improvement with this system is available. Data reduction from the large number of experiments is continuing. A most important difference sought and observed with the different growth surfaces relates to epitaxial growth potential for this system. The crystalline structure of the diol crystals grown from solution is dominated by hydrogen bonding between hydroxy groups. This prevents the diacetylene units from achieving their maximum interaction and is thought to lead to fragile crystals. We find that a glass surface seems to attract hydrogen bonding to the glass surface and hence the intramolecular hydrogen bonding, at least in the first monolayer, is different. The difference in the growth patterns, which may signal a morphological difference is apparent from observing the initial buildup pattern of the films. With the glass surface the film growth is continuous from the beginning. With the polyethylene surface growth occurs in small crystallites evidence of growth being favored by building on prior nucleation sites. With copper there seems to be a buildup of prior nucleation sites but the growth is not as dramatic as with polyethylene. These studies are continuing with the goal of incorporating our present best film-forming system into a Get Away Special experiment.

## Bibliography

1. (a) H. J. Caulfield et. al., eds., Special Issue of Proc. of IEEE, July, 1984; (b) D. Psaltis, ed., Special Issue of Opt. Eng., Jan, 1984; (c) J. Neff, ed., Special Issue of Opt. Eng., Jan, 1985; (d) D. J. Williams, ed, "Nonlinear Optical Properties of Organic and Polymeric Materials", Washington: Amer. Chem. Soc. Symposium Series No. 233, 1983.
2. B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch, and J. L. Bernstein, J. Appl. Phys., 50, 2523 (1979); G. F. Lipscomb, A. F. Garito, and R. S. Narang, J. Chem. Phys., 75, 1509 (1981).
3. C. Sauteret, J. -P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. H. Baughman, and R. R. Chance, Phys. Rev. Lett., 36, 956 (1976).
4. G. Wegner, Z. Naturforsch., 24B, 824 (1969); Makromol. Chem., 145, 85 (1971); ibid., 154, 35 (1972); for a review, see D. Bloor in "Developments in Crystalline Polymers", D. C. Bassett, Ed., Appl. Science Publ., London and New Jersey, 1982, 151.
5. V. Enkelmann and G. Wegner, Angew. Chem., 89, 432 (1977); unpublished work of V. Enkelmann (1983) cited by M. Schwoerer and H. Niederwald, Makromol. Chem., Suppl. 12, 61 (1985).
6. D. Kobelt and E. F. Paulus, Acta Cryst., B30, 232 (1974).
7. A. F. Garita in ref. 1d.
8. R. H. Baughman, J. Polym. Sci., Polym. Phys. Edit., 12, 1511 (1974).
9. M. Thakur and S. Meyler, Macromolecules, 18, 2341 (1985).
10. G. M. Carter, M. K. Thakur, Y. J. Chen, and J. V. Hryniewicz, Appl. Phys. Lett., 47, 457 (1985).
11. B. J. Orchard and S. K. Tripathy, Macromolecules, 19, 1844 (1986).
12. C. L. Cook, E. R. H. Jones, and M. C. Whiting, J. Chem. Soc., 2883 (1952).